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## **Determination of Anhydrite in Reservoirs for EOR**

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### **Abstract**

Alkali in surfactant flooding can sequester divalent ions and reduce surfactant adsorption. When the alkali is sodium carbonate and anhydrite (or gypsum) is present, the anhydrite will dissolve and precipitate as calcium carbonate. An anhydrite level of only 0.1% in the rock is enough to retard the breakthrough of a 1% sodium carbonate solution by approximately 0.7 pore volume, which would greatly reduce effectiveness of a process having surfactants sensitive to divalent ions. Different alkalis will also react with anhydrite.

A methodology is presented to estimate the amount, if any, of anhydrite present in the reservoir. The method is based on brine software analysis of produced water compositions and inductively coupled plasma (ICP) analysis of core samples. X-ray powder diffraction (XRD) can detect anhydrite when it is abundant, but will not be able to detect the low amounts that can still be harmful to chemical EOR.

Produced water and core samples were analyzed from a high-temperature, high-salinity carbonate reservoir, which is a candidate for surfactant EOR. Ten water analyses were obtained from ten wells in five formations. The formation brines ranged from 3-to-20% of TDS. The reservoir rock was mostly dolomite, and reservoir temperature was about 120°C. The saturation index calculated for all formation waters at high salinity (higher than sea water) was positive, indicating over saturation with anhydrite. The saturation index was calculated with ScaleChem for high salinity and PHREEQC, which is limited to lower salinity. The elemental composition of rock samples dissolved in acid was determined by ICP. The mass percent of anhydrite was computed from the elemental analysis.

When these methods were applied to the dolomite reservoir of interest, they strongly indicated that anhydrite was present in sufficient amounts to preclude use of sodium carbonate in a surfactant recovery process.

### **Introduction**

The advantages of the use of alkali in anionic surfactant formulations for EOR applications are well known. Previous experiments have demonstrated gravity-driven enhanced recovery of oil when interfacial tensions are low following spontaneous imbibition of such formulations into oil-wet carbonate rock Hirasaki (2004). Studies conducted by Seethepalli *et al* (2004) have shown that the use of anionic surfactants in presence of sodium carbonate can not only reduce oil-brine interfacial tension but also change wettability from oil wet to intermediate/water-wet conditions for carbonate surfaces (i.e. limestone, marble, dolomite and calcite). In these previous studies, some common reasons to use sodium carbonate are listed: The high pH produces natural surfactants in-situ by the reaction with the naphthenic acids in the crude oil. The carbonate suppresses the concentration of calcium in the brine. Sodium carbonate reduces ion exchange, mineral dissolution, and adsorption of anionic surfactants. The carbonate precipitates do not exacerbate permeability compared with silicates and hydroxides. Moreover, sodium carbonate is inexpensive.

Presence of anhydrite is unfavorable in flooding with surfactants with low tolerance to divalent ions (e.g. calcium and magnesium), Alkali in surfactant flooding sequesters divalent ions and reduces surfactant adsorption. When the alkali is sodium carbonate and anhydrite or gypsum is present, the anhydrite will dissolve and precipitate as calcium carbonate. Anhydrite or gypsum at a level of only 0.1% in dolomite rock with porosity of 23% is enough to retard the breakthrough of a

1% by mass sodium carbonate solution by 0.7 pore volume as indicated in fig 1 and fig 2. The analysis for fig.1 is consistent with results reported by Liu (2008). Different alkalis will react as well with anhydrite.

The analysis of figs.1 and 2 is based on the assumption that anhydrite will consume the sodium carbonate, producing a precipitate of calcium carbonate (Hirasaki, 2005 and 2006).

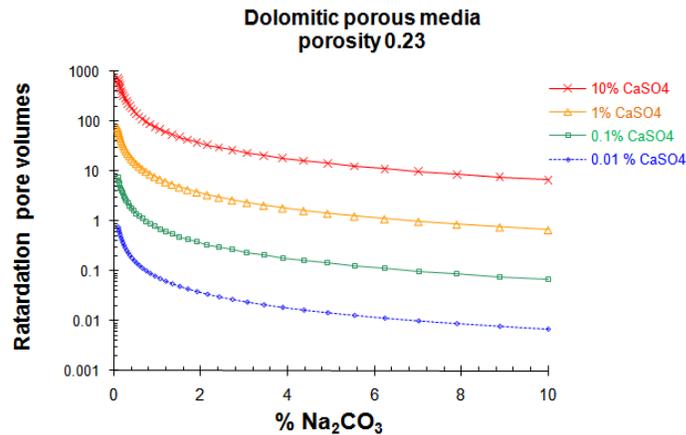
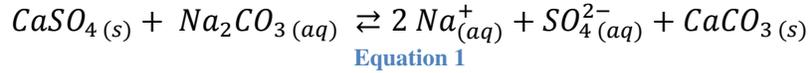


Figure 1 Relationship of the retardation time and mass percentage of CaSO<sub>4</sub> in dolomite rock

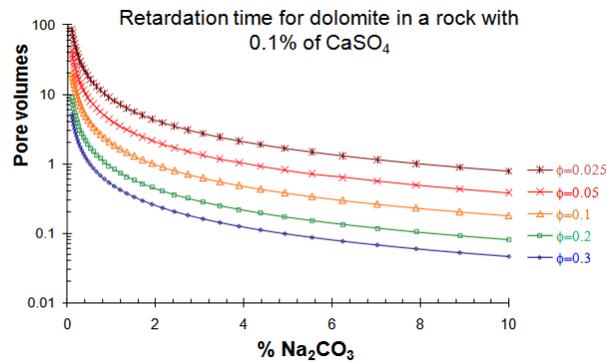


Figure 2 Relation of retardation time and porosity of the rock; the effect worsens for less porous media.

The retardation of sodium carbonate in a formulation may be as much as several pore volumes if the concentration of sodium carbonate is below 1%, and the effect is increased if the concentration of anhydrite is higher (fig.1) or if the porosity of the rock is lower (fig.2). Thus, even small proportions of anhydrite are important in designing an EOR formulation if use of sodium carbonate is to be considered.

The objective of this study is to develop a tool to predict the presence of anhydrite in a formation, and to employ the tool for a particular formation as an example of its applicability. The basic idea is to collect the information from the reservoir's water analysis and use it with available brine software to see if the water was in contact with the solid minerals of interest, in this particular case with anhydrite. A second method is direct analysis of core samples using inductively coupled plasma (ICP).

### Information about the sea water and formation brines

In this study the salinity of the local sea water was higher than a typical sea water (DOE, 1994); the percentage excess of the main ions may be seen in fig.3. Figs. 4a and 4b indicate the concentrations of the different cations and anions in the wells sampled in the study (wells may belong to the same or different reservoirs or the same or different geological formations).

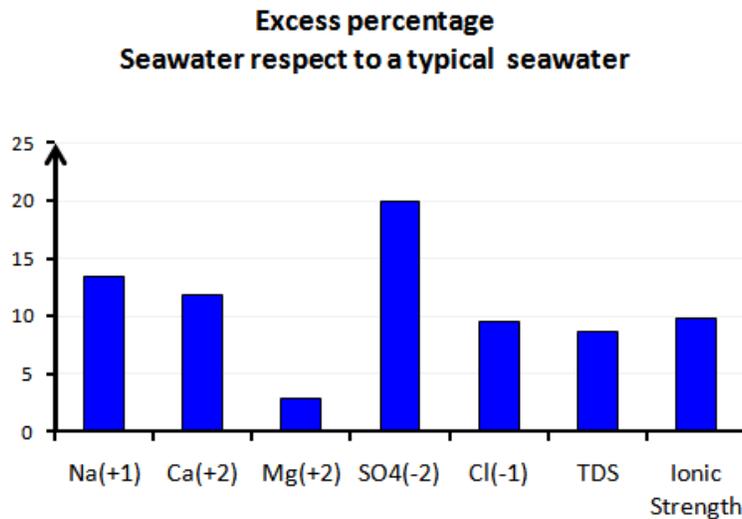


Figure 3 Excess of the main ions respect tro typical sea water and ionic strength.

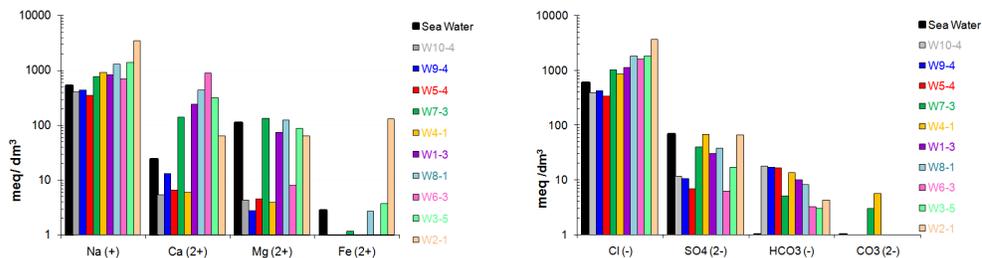


Figure 4a (left) and 4b (right) indicate the composition of the water for the different wells in this study. Fig. 4a is for cations and fig. 4b is for anions expressed in mili-equivalents per liter.

One of the main characteristics of the different water analyses is that the concentration of sulfates is less than the concentration of sulfates in sea water (fig. 4b), but the concentration of calcium is higher in most of the formation brines from the wells (fig. 4a) than in sea water. The alkalinity is also higher in the brines than in sea water. This higher alkalinity is important in the solubility of different minerals, but not controlling in the saturation with respect to calcium sulfate. The analysis of the sea water is important if it was used in the drilling process. If the water used in the drilling process is over saturated in any mineral, it may precipitate in pore space near the well and mislead the analysis of the rock if core material is extracted for analysis. False positive with respect to a mineral may change the strategy of tailoring surfactants for a specific EOR application, increasing the final cost of the process.

The first approach to solve the task was to verify the saturation of different minerals in the water samples and to use applicable software to predict the thermodynamic properties of the brines and whether they are in equilibrium with solid phases.

## Description and validation of software:

Different software can be used to predict the thermodynamic properties of brines. Each type of software has pros and cons, but in this study the main interest is precise prediction of saturation level of components, in order to infer if calcium sulfate is or is not present in the formation.

To successfully use any software, a complete water analysis is needed. The concentration of the cations and anions is needed as well as the pH and the alkalinity of the sample. If the pH and alkalinity are not known, the analysis can still be performed if the concentration of dissolved gases is known (e.g. CO<sub>2</sub>, H<sub>2</sub>S, etc.), or if the partial pressure of the CO<sub>2</sub> in the gas phase in equilibrium with the brine is known. It is required to know the temperature and the pressure of the reservoir and to know the exact conditions when the water analysis was done. Any depressurization of the sample or release of CO<sub>2</sub> to the atmosphere will change the calculation, as well as exposing the water sample to an atmosphere containing carbon dioxide.

Initially two software packages were selected to be used during the study (PHREEQC and ScaleChem), but a third option was later included for comparative purposes (ScaleSoftPitzer), because some inconsistencies with respect to the database were found in the Pitzer model with PHREEQC. The third software package was used to verify the performance of PHREEQC once the database was modified.

ScaleChem is very flexible and complete software, but is licensed software. PHREEQC is free software, but presented no consistency with respect to the database for the activity model parameters and for the solubility products. It is recommended that users of a software package be familiar with the activity models used and with the available database. PHREEQC has the advantage that the data base can be viewed and modified, and it has the advantage of being an open code. PHREEQC is recommended for experienced users to make preliminary studies because the code can easily be modified to take into account variables not obvious at first glance like the pressure. However, this tool must be evaluated for the system under consideration.

Most of the commercial software uses the activity model proposed by Pitzer, and this was the model selected to be used with the software PHREEQC. In this model the activity coefficient requires two contributions. One is the long-range contribution, which uses the extended Debye-Huckel term (the first term of the right hand side of equation 2). The other is the short-range contribution, which has the extra virial coefficients with respect to molality, as indicated in the last two terms on the right hand side of equation 2.

$$\ln \gamma_{\pm} = -A_P |z_+ z_-| + B_P^{2-2} m \frac{2\nu_+ \nu_-}{\nu} + C_P m^2 \frac{2(\nu_+ \nu_-)^{3/2}}{\nu}$$

Equation 2

$$A_P = A \left[ \frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} + \frac{2}{b} \ln(1 + b\sqrt{I_m}) \right]$$

Equation 3

$$B_P^{2-2} = 2\beta_0 + \frac{2\beta_1}{\alpha_1^2 I_m} [1 - [1 + \alpha_1 \sqrt{I_m} - 0.5\alpha_1^2 I_m] \exp(-\alpha_1 \sqrt{I_m})] \\ + \frac{2\beta_2}{\alpha_2^2 I_m} [1 - [1 + \alpha_2 \sqrt{I_m} - 0.5\alpha_2^2 I_m] \exp(-\alpha_2 \sqrt{I_m})]$$

Equation 4

Parameters for these equations can be found in Lee (2008) and Ott and Boerio-Goates (2000). No consistency was found in the Pitzer database used by PHREEQC. Parameters for calcium sulfate coincided with Ott and Boerio-Goates, but for magnesium sulfate the data were extracted from Lee. Another inconsistency of the database was the solubility product, but the database was modified using the tables reported in Stumm and Morgan (1996). If the software does not include the effect of pressure, this can be added by modifying the database of the solubility product to include the pressure effect. For anhydrite the parameters can be found in Monnin (1990), and the correction is obtained with equation 5:

$$\ln K_{SP} = \ln K_{SP}^0 - \frac{\Delta V_r^o}{RT} (P - P_o) - \frac{\Delta K_r^o}{2RT} (P - P_o)^2$$

Equation 5

Three different tests were used to select the software packages for this study. The first test is to see if they agree with experimental data in the trend of saturation temperature with respect to anhydrite in a process in which sulfate is removed from sea water. Sea water is used in this initial simulation because we need to know whether we can inject sea water in the proposed EOR process for the reservoir of interest without having precipitation of any salts. A second test is to verify if the software can predict the solubility of calcium sulfate in deionized (DI) water at different temperatures. A third test is to calculate the solubility of calcium sulfate in highly salty water (ca. 20% of NaCl). The results of these tests are presented in figs. 5-7. All three of the above software packages predict more less the same results for water systems at low salinity (i.e. salinity close or less than sea water), but differences can be found at high salinity (between sea water and 20% of sodium chloride). For this reason a validation of the software was required.

As indicated above the three packages were used to compare predicted changes in the saturation temperature of anhydrite as different percentages of sulfate were eliminated from sea water. The three predicted similar trends, as indicated in fig. 5, but the difference in predictions increased as more sulfate was replaced by chloride.

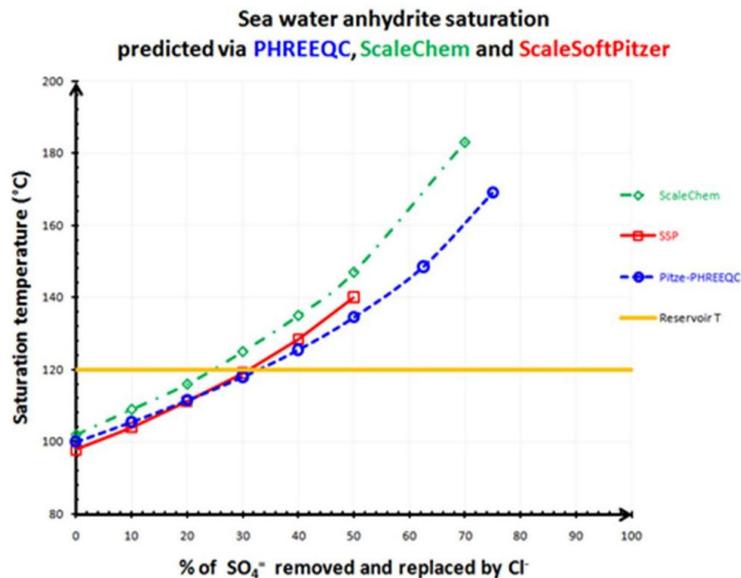


Figure 5 Saturation temperature respect to anhydrite for the sea water once the sulfate is removed in different proportions. Temperatures higher than the values delimited by the curve are for over saturated samples, below the curve the sample is undersaturated.

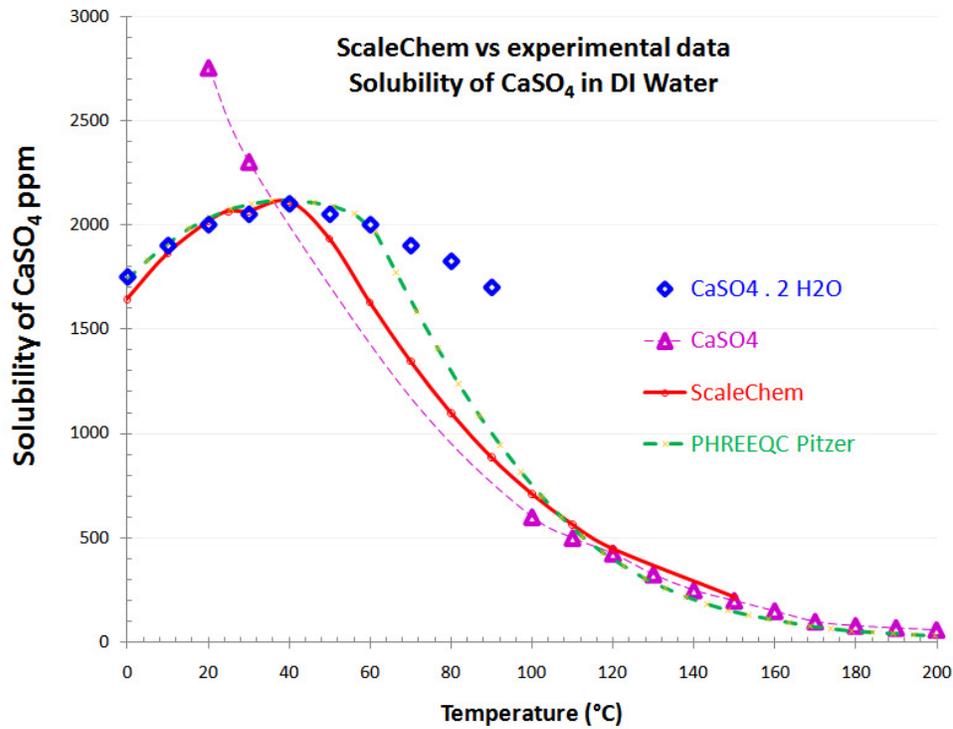
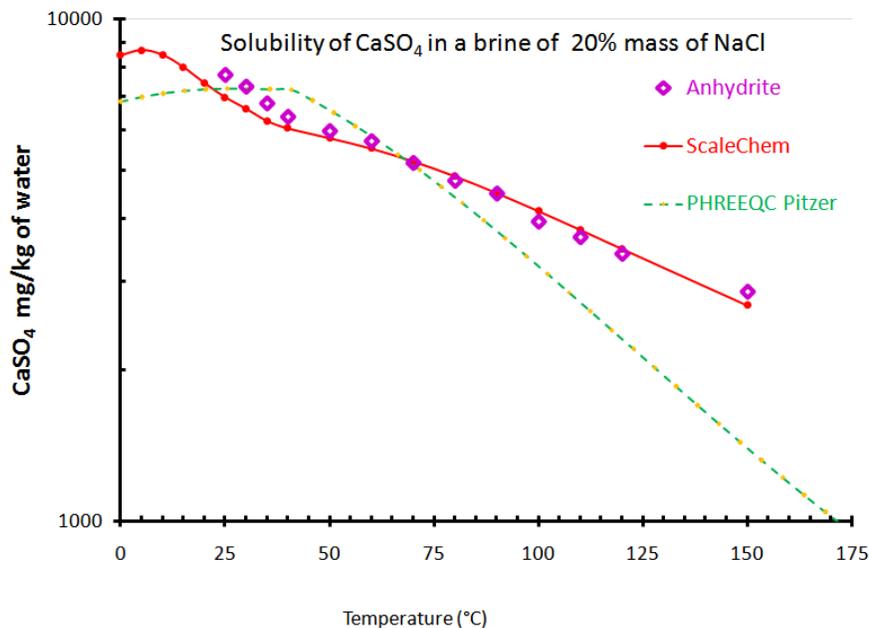


Figure 6 Prediction of the solubility of calcium sulfate at different temperatures using ScaleChem and PHREEQC at 1 atm or saturation pressure for temperatures higher than the normal boiling point for water. For the software PHREEQC the database pitzer was used, but the parameters for the solubility product equation for anhydrite were updated.



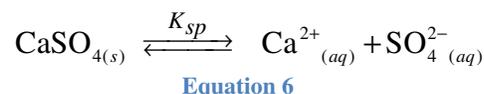
**Figure 7 solubility of calcium sulfate in a 20% mass NaCl brine at different temperatures. The experimental values are averages of different authors reported by Blount and Dickson (1973)**

Fig. 6 indicates that the error in region between 50° and 100° is less when ScaleChem was used to predict anhydrite solubility for DI water. ScaleChem is also better for the 20% NaCl solutions of fig. 7, especially for temperatures above 90°. More details about the analysis of the robustness of the different software, pros and cons, and important observations are discussed in the appendix, and the effect of pressure is shown as well. Fig.7 was constructed using experimental values from Partridge *et al* (1927), and good agreement was found using ScaleChem; the error is higher using PHREEQC. To minimize the error shown in fig.7 using PHREEQC the Pitzer database was used but a revision was needed for solubility product of anhydrite. For high salinity the comparison was done using the experimental data reported by Blount and Dickson (1973). The extremes of solubility in DI water and 20% of NaCl cover the spectrum of the content of sodium chloride of the formation brines analyzed in this study.

Oli Systems (2011) presented an exhaustive comparison of experimental data vs predicted results from ScaleChem, not only for the systems analyzed in this article, but for a large number of chemical species. Their extensive database can be used as a reference for additional validations.

## Methodology

For each water analysis related to a specific well studied (each well belongs to different reservoir and formation) a thermodynamic analysis was done, calculating the saturation index for all the different chemicals. The saturation index for a solid mineral is defined as departure from equilibrium:



The saturation ratio is the relationship between the actual activities product and the solubility product (which is the activity product that can be obtained at equilibrium), as shown here for anhydrite:

$$SR = \frac{a_{Ca^{2+}} a_{SO_4^{2-}}}{K_{sp}}$$

Equation 7

Then the saturation index is a logarithmic scale of the saturation ratio defined as:

$$SI = \log_{10}(SR)$$

Equation 8

Using this definition of saturation index, a negative value will be obtained for under saturated brines, zero for saturated brines and, and positive values for oversaturated brines. Saturation and oversaturation of a mineral may be an indicator of the presence of that species in the formation.

After calculation of thermodynamic preoperties of the different water analysis, core materials from different wells were analyzed using XRD and ICP to verify the predictions of the software. Additional tests were done to verify if nondestructive tests to rock material are possible. The rock was contacted with brine without sulfates at high temperature to measure solubilization of anhydrite via ICP.

## Results

For ten different wells the saturation index with respect to anhydrite was calculated at different temperatures. Results are summarized in fig.8

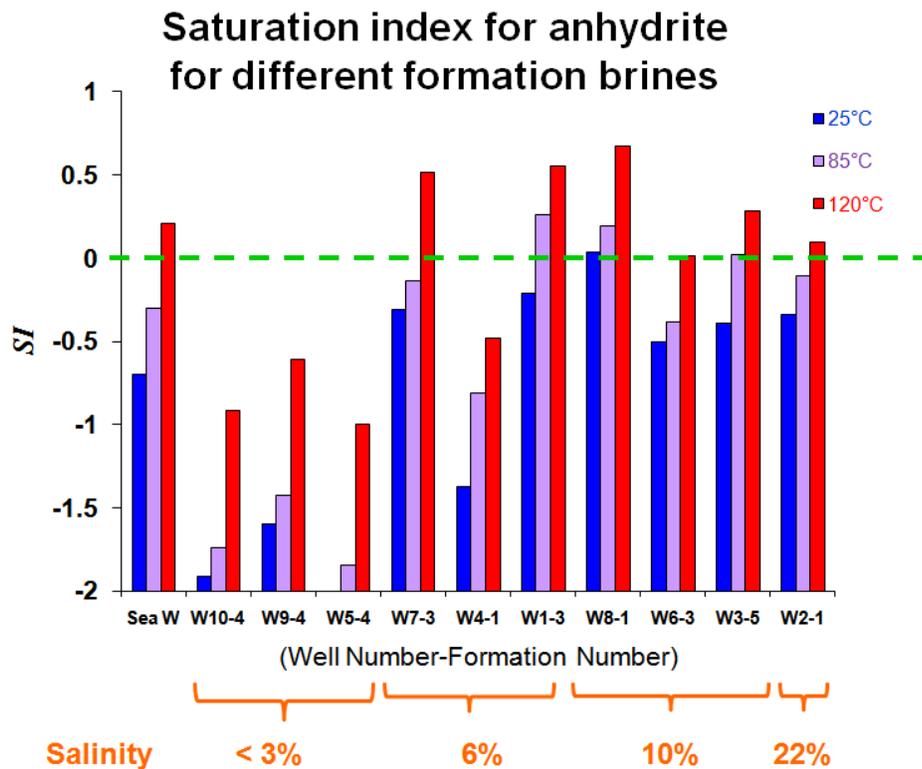


Figure 8 Saturation index for several wells, in different formations at room temperature, 85°C and reservoir temperature (120°C). The green line indicates the saturation limit, higher values are oversaturation

Most of the formation brines from the reservoirs of interest in our design for EOR are between 6% and 10% of total dissolved solids. The thermodynamic analysis in fig. 8 indicates that at reservoir temperature of 120°C these brines are saturated or oversaturated in anhydrite. Formation brines with salinity less than the salinity of sea water during the initial analysis presented undersaturation, but after detailed revision of the information for those wells, most of them were saturated

or close to saturation. However, the analysis was strongly dependent on the depth of those samples (i.e. the formation), and a specific case is presented in the appendix (fig.A-19), where the salinity was low, but oversaturation existed.

The saturation index for most of the minerals is sensitive to the pH, anhydrite being an exception. The effect of the pressure should be considered for very high pressures, especially those samples close to saturation. In our system the pressure had a weak effect, no more that 4°C of difference in anhydrite saturation temperature for changes in pressure close to or higher than the reservoir pressure.

Different experimental techniques can be used to detect the presence of anhydrite in the rock, but this can be a problem when concentration of calcium sulfate is not high in the formation. To verify if anhydrite is one of the minerals present in the formation, X-ray powder diffraction is one alternative, but this technique may fail if the concentration of the anhydrite is less than 1%. Moreover, detection can be more difficult if the rock has more than three different minerals. Another technique consists of weighing a sample of 2 g and contacting with 0.5 of DI water for 12 h. After separating the aqueous phase, one precipitates the  $\text{SO}_4^{2-}$  of the dissolved anhydrite using  $\text{BaCl}_2$  and weighs the  $\text{BaSO}_4$  formed. However, the detection limit is 0.6 wt% in the sample, according with Paulict *et al* (2005). This value is not low enough for the method to detect all anhydrite contents that could significantly affect alkali/surfactant EOR processes, as indicated in the earlier discussion of figs. 1 and 2.

A sample from one of the formations was cleaned with tetrahydrofuran (THF) and after that with chloroform-methanol azeotropic mixture. Then it was dried and ground in a shaker box before the X-ray powder diffraction. Fig.9 shows the sample, after being cleaned (left) and after being ground (right).



Figure 9 Sample from a carbonate reservoir before and after treated in the shaker box.

Zoom of the XRD close to the highest peak of anhydrite for F1A, anhydrite and dolomite

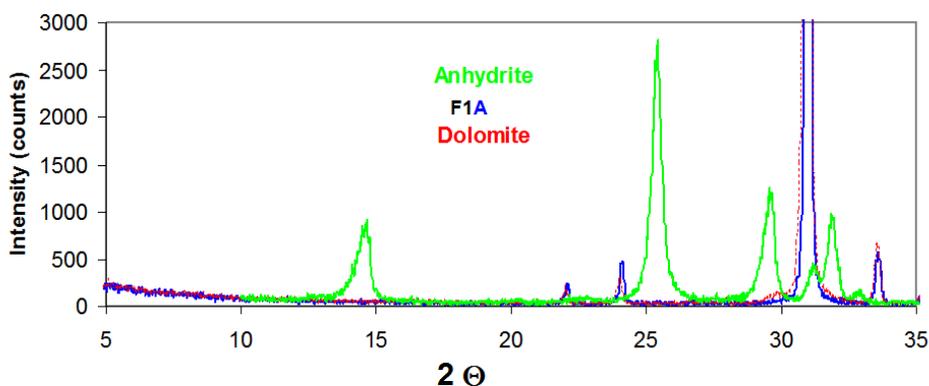


Figure 10 zoom of a section of the response of the intensity for three different samples; anhydrite (reference 1), for the sample labeled (F1A) and dolomite (reference 2)

Fig. 10 compares the response of the rock sample vs. two references; dolomite and anhydrite. This methodology was not conclusive about the presence of anhydrite in the sample. It is useful only for concentrations of anhydrite higher than 2%

when more than two minerals are present; this detection limit was suggested by Alai *et al* (2005). The complete comparison can be found in the appendix. The apparatus used was the Rigaku D/MAX 2100 Ultima II Powder diffractometer.

Inductively coupled plasma (ICP) was used to confirm the composition of the rock (Perkin–Elmer Optima 4000 DV, Atlanta, GA, USA). A sample between 4 and 5 g of the rock was dissolved in HCl (1N) using between 120 and 150 ml. The process of dissolution took more than 24 h. After 2 days the sample was diluted in a proportion 1 to 1000 using nitric acid 2%, then filtered using 0.2  $\mu\text{m}$  syringe filter before the measurement. All the samples tested were soluble in the 1N HCl.



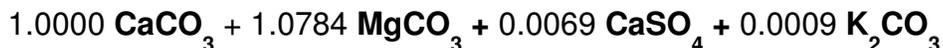
**Fig. 11** sample before trimming (upper image), before cleaning after being cut (bottom left), and after the cleaning process (bottom right). Sample was dissolved in between 10% to 50% excess (assuming dolomite) of hydrochloric acid (1 N), and analyzed via ICP after dilution 1/1000 in aqueous solution at 2% in  $\text{HNO}_3$

The results from ICP for this sample are given in table 1. They confirm the presence of anhydrite and provide the composition of the rock as well.

**Table 1** Elemental analysis of the rock after ICP

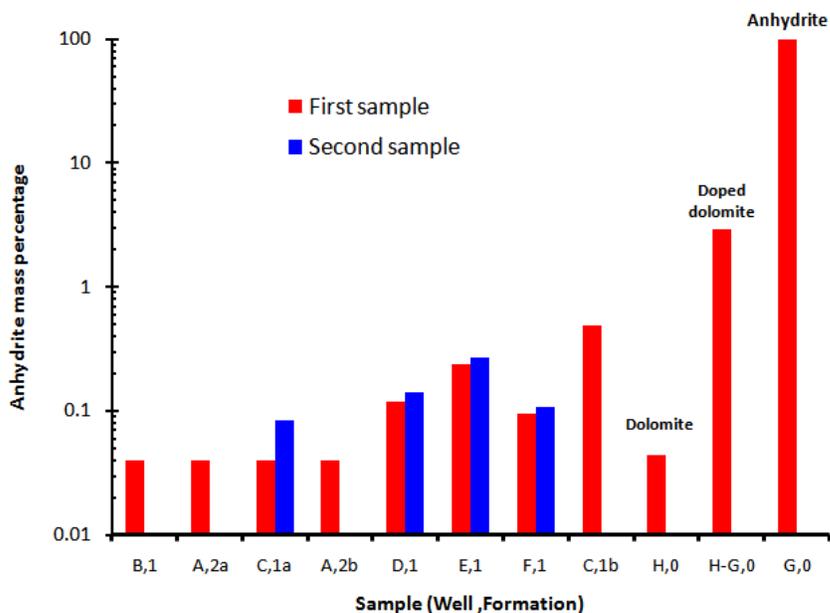
Element	$\text{mg/dm}^3$ (milligrams per liter)
Ca	7.490
Na	0
S	0.04
Fe	0
Mg	4.866
K	0.013

Using this elemental analysis as representative of the rock, the rock has the chemical form (on a molar basis):



This represents ca. 0.49% (mass base) of anhydrite, which is large enough to be important to consider for sodium carbonate consumption (Hirasaki *et al* 2005 and 2006)

Additional samples were analyzed for anhydrite content using the same methodology. The results are summarized in fig.12.



**Figure 12 Samples of rock formation, dolomite used in adsorption experiments, and doped dolomite. All of them presented anhydrite.**

Samples (B,1), (C,1), (D,1), (E,1) and (F,1) are from rocks of different wells but the same kind of formation.

Samples (C,1a) and (C,1b) are from the same well, the same formation, but from different parts of the core.

Sample (H,0) was commercial dolomite powder used as material to run a control experiment. The control sample which was labeled as sample (H-G,0), is a mixture of commercial dolomite (H,0) doped with anhydrite (G,0) and the concentration measured via ICP coincides with the proportions used to make it.

All the samples were in the range of calibration for the ICP apparatus, and every three samples a quality control sample was measured as well.

Sample rocks that seemed heterogeneous by naked eye presented no more than one order of magnitude difference in anhydrite percentage, for example samples (C,1a) and (C,1b) in fig.12.

Additional samples were contacted with formation brine, replacing the sulfate with an equivalent amount of Cl<sup>-</sup>. After a week of equilibration at 90°C, these water samples were analyzed by ICP using dilutions of 1 to 2 and 1 to 3 with HNO<sub>3</sub> 2%. Small, adjacent samples from a piece of core material showed total agreement with respect to sulfate content (42.42 g of rock contacted with 200 ml of brine without SO<sub>4</sub><sup>2-</sup>). Thus, nondestructive tests can be used to quantify anhydrite, but the content of anhydrite must be considered in the design of the test when the content of anhydrite is high. The software used in this study was used in the design of the experiment to make sure that complete dissolution of anhydrite occurred.

## Conclusions

Thermodynamic analysis of formation brines with existing brine software can be used to calculate saturation index of minerals in a reservoir and, in particular, determine whether anhydrite is present in the formation. However, the analysis cannot determine the amount that is present..

XRD lacks the sensitivity to detect whether anhydrite is present in formation rocks at low concentrations which would produce detrimental effects on alkali/surfactant processes.

In contrast, ICP using a solution of dissolved rock in 1N hydrochloric acid was a reliable method. It was able to measure not only the content of anhydrite, but also the overall composition of the rock and the proportions of different minerals

ICP was also used to measure the presence of anhydrite in a rock sample nondestructively by equilibrating it with a formulated brine at a specific temperature for several days. The brine formulation and equilibrium conditions were set in order to achieve reliable results, i.e. to assure that the brine could dissolve all the anhydrite present without becoming oversaturated.

## Nomenclature

$A$  Debye-Hückel virial coefficient, specific for the solvent ( $A=A_1=3A_0$ , Bradley and Pitzer, 1979)

$A^{z-}$  Anion and its charge

$a_p$  Activity of the ionic species  $p$ ,  $a_p = [P] \gamma_p$

$B_p^{2-2}$  Second virial coefficient for 2:2 Electrolyte.(e.g.  $CaSO_4$ , Lee, 2008)

$b$   $b=1.2$  with units of  $(Im)^{-1/2}$

$C^{z+}$  Cation and its charge

$C_p = (3/2) C^\phi$  (Lee, 2008)

$Im$  Molal ionic strength (gmol/ kg of water)

$K_{SP}^o$  Solubility product at atmospheric pressure. (i.e. equilibrium constant at 1 bar).

$K_{SP}$  Solubility product or equilibrium constant

$m$  molality (gmol/ kg of water)

$P$  Pressure (Pa)

$P_o$  Atmospheric pressure

$[P]$  Concentration of ionic species  $P$  (e.g.  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ , etc.)

$R$  Gas constant (8314.34 J /kmol-K)

$SI$  Saturation index

$SR$  Saturation ratio

$T$  Temperature (K)

$z_+, z_-$  charge of the cation (positive) and anion (negative) respectively, valences of ions.

$\alpha_1$   $\alpha_1=1.4$

$\alpha_2$   $\alpha_2=12.0$

$\alpha$   $\alpha=2$  ( $\alpha_1=\alpha$  and  $\alpha_2=0$  if the electrolyte is 1:1, 1:2 or 1:3)

$\beta_0, \beta_1, \beta_2$  and  $C^\phi$  are parameters specific to the ionic species

$\gamma_{\pm}$  Mean activity coefficient  $\gamma_{\pm} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu}$

$\Delta V_r^0$  The change of the standard partial molal volume for the mineral dissolution

$\Delta K_r^0$  The change of the standard compressibility of the dissolution reaction

$\nu_+, \nu_-$  ( $C_{\nu_+} A_{\nu_-} = \nu_+ C^{z_+} + \nu_- A^{z_-}$ ) Proportion of the cation and anion in the mineral or salt,  $\nu_+ z_+ + \nu_- z_- = 0$

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**Appendix A**

XRD results

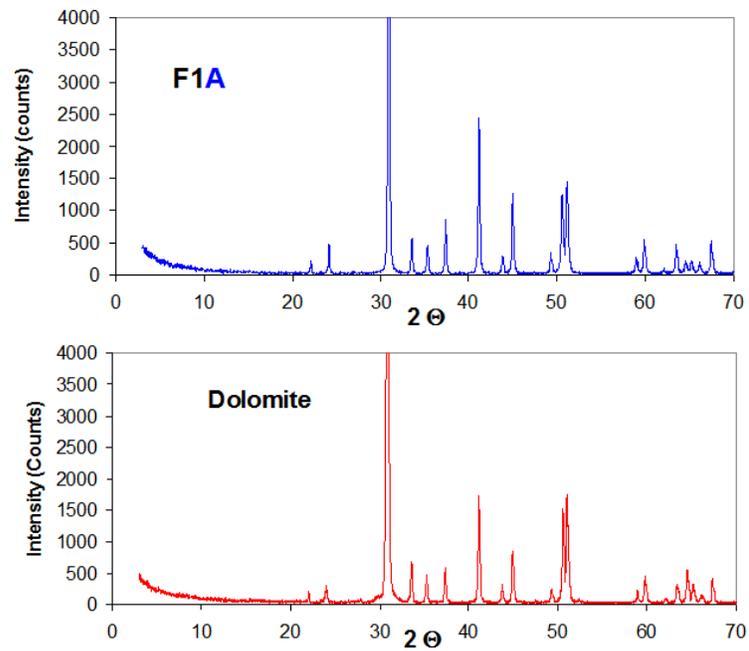
**XRD response to sample F1A**

Figure A-1 Intensity response of the powder XRD from a rock sample (F1A, blue) and a sample of dolomite (red )

## XRD response to sample F1A

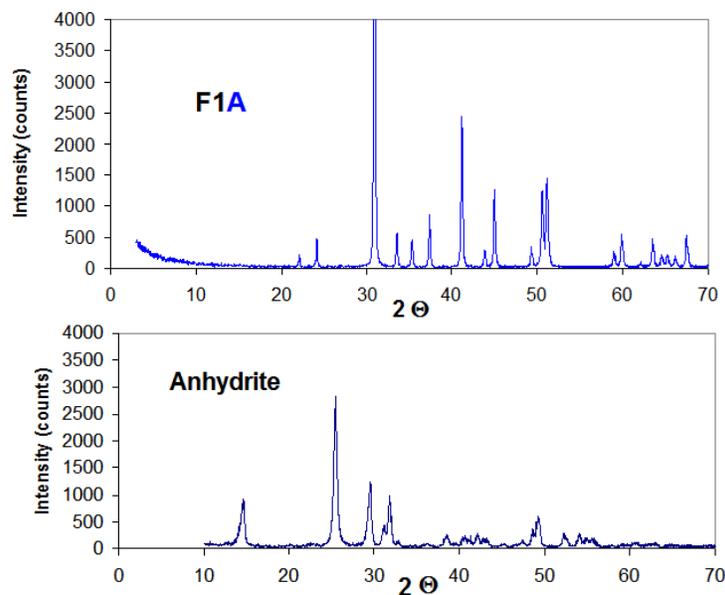


Figure A-2 Intensity response of the powder XRD from a rock sample (F1A, blue) and a sample of anhydrite (dark blue )

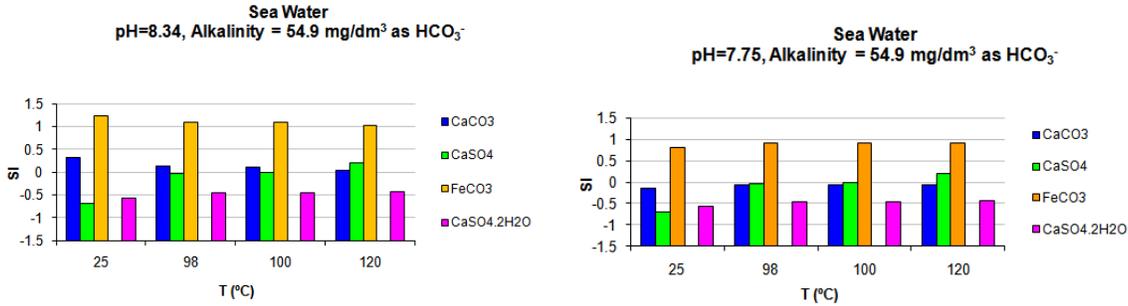
Examination of fig.A-1 and fig.A-2 helps to conclude that the content of anhydrite in the sample is too low to be detected using this technique. Using zooms of the zone where the maxima of the different components (dolomite and anhydrite) are located was not enough to confirm the presence of anhydrite peaks (see fig. 10).

### Analytical methods

Solution phase or the dissolved rock in solution, the total Ca, Na, S, Fe Mg and K concentrations were measured by ICP (Perkin–Elmer Optima 4000 DV, Atlanta, GA, USA). Ca and Na were detected at 371.933 and 589.59 nm wavelengths, respectively, with ICP. ICP was calibrated at 0, 0.2, 1.0 and 5.0 ppm for Ca, 0, 2, 10 and 50 ppm for Na. Fe, Mg, K and S were detected at 238.204, 285.213, 766.49 and 181.975 nm wavelengths, respectively, with ICP. ICP was calibrated with 0, 1, 5 and 25 ppm for all of them (i.e. Fe, Mg, K and S). Yttrium (Y) was used as the international standard for ICP calibration. Excellent linear calibration was generally observed with a correlation coefficient higher than 0.9999. A quality control sample was analyzed every three samples to insure that the calibration was valid for the analysis. The detection limit was 0.01 mg/L for ICP and the relative standard deviation of three replicate analyses was generally below 3%.

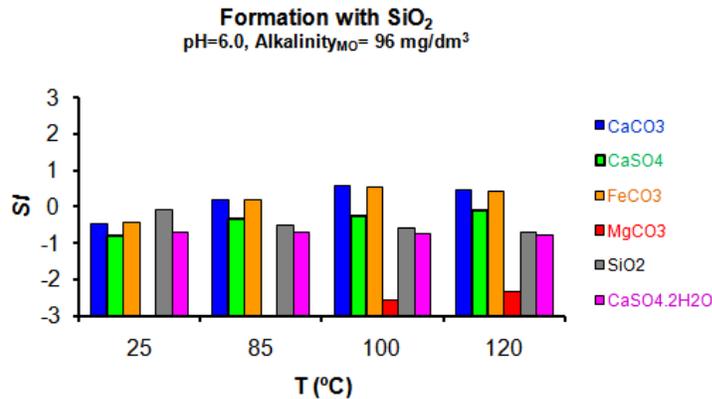
### Water analysis

It is important to have reliable and complete information about the water from the reservoir. The pH and alkalinity are variables that affect the results of the saturation index for most of the minerals of interest. However, in the particular case of anhydrite, the effect of alkalinity and pH are almost negligible.



**Figure 13 Comparison of saturation index for a sea water with different pH. The saturation of anhydrite is not affected by the hydrogen potential, but the saturation of calcite at low temperature has a strong effect in saturation, this effect can be seen over siderite as well.**

This behavior is shown in fig. A-3, where it may be seen that at low temperature (25°C) the saturation index of calcium carbonate strongly depends on pH, but the saturation index of anhydrite stays about the same. Similar comments can be made for the higher temperatures. The effect of temperature on calcium carbonate saturation index changes from one pH to the other. For this sea water if the pH is 7.75, the brine is unsaturated in calcium carbonate, but it will be oversaturated if the pH is 8.34. Hence it is important to know with precision the values of the alkalinity and pH, or know the pH and the partial pressure of CO<sub>2</sub> in equilibrium with the brine, or know the partial pressure of CO<sub>2</sub> in the atmosphere in contact with the brine when the analysis was made.



**Figure A-4 Saturation index of a formation brine with high content of silica. For this formation the saturation limit respect to anhydrite is 120C. For this case the temperature is important.**

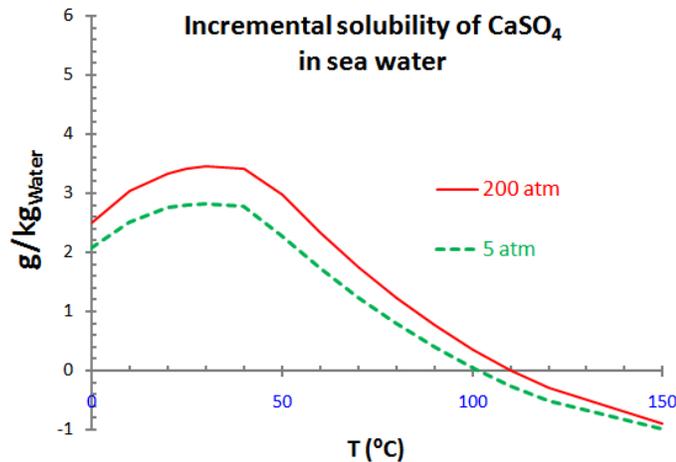


Figure A-5 Incremental solubility of the sea water at low and high pressure. Incremental solubility is the additional calcium sulfate that can be added to the sea water. The sea water of this study already has 1.615 g of calcium sulfate per kilogram of water. Above the curve of incremental solubility the sample will be oversaturated.

Pressure is another variable that must be considered in the analysis, but little effect was found respect to anhydrite saturation index. Figure A-5 shows that by increasing the pressure from 5 atm to 200 atm or approximately 3000 psi, an increment in saturation temperature of 4°C is predicted. This small temperature increment is not enough to produce solubility of anhydrite in sea water at reservoir temperature. The actual reservoir pressure is only about 130 atm or 1900 psi.

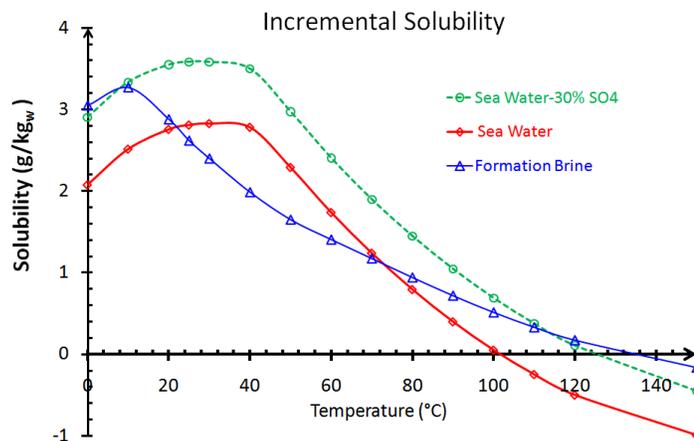
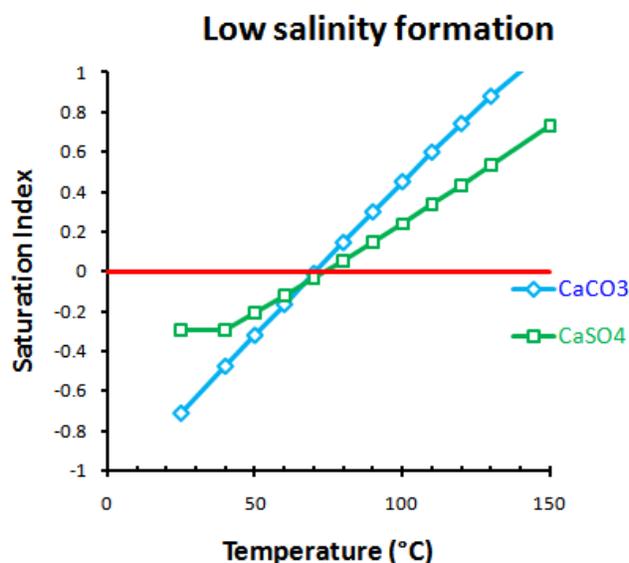


Figure A-6 Incremental solubility of the synthetic formation brine used in the experiments during core flooding. Incremental solubility of the sea water, and the Incremental solubility of the treated sea water (i.e. replacing 30% of sulfates)

For laboratory experiments the synthetic sea water cannot be used at temperatures higher than 100° C, in order to do that 30% of the sulfates need to be replaced, in this simulation 30% of sulfates were replaced by chlorine ions and its corresponding divalent ions (Ca and/or Magnesium) were replaced by sodium ion in the same proportion. The synthetic formation brine presented no problem of saturation respect to anhydrite.

For qualitative purposes any software can be used to see trends in the effects of the variables like, pressure, salinity, pH, alkalinity and even the effect of ions, but for precision is required to have a software able to fit parameters to experimental data, and to be familiar with the activity models in order to select the one that will model you system. Software like

ScaleSoftPitzer has features that will let you analyze the effect of using scale inhibitors, but is limited for the Pitzer activity model and was designed for special applications. PHREEQC is a free software and can be modified, but is recommended to verify the database for the salts and minerals of interest, and it limited by the activity model which is the extended version of Debye-Hückel that works at low salinity, it also has the database to use the Pitzer model, but its database is limited and can not predict the concentration of ion pairs with the Pitzer model.



**Figure 14** Most of the formations at low salinities (i.e. less than 4% of TDS) may be oversaturated with anhydrite, if calcium content in the sample is high. For this case the concentration of the ions are:  $\text{Na}^+=11638$  mg/l,  $\text{Ca}^{2+}=2800$  mg/L,  $\text{Mg}^{2+}=559$  mg/L,  $\text{Fe}^{2+}=20$  mg/L,  $\text{Cl}^-=23660$  mg/L,  $\text{SO}_4^{2-}=1120$  mg/L,  $\text{HCO}_3^{2-}=120$  mg/L, and pH=6. The red line is the saturation limit.

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